

PROCESS FOR PREPARATION OF EPOXYDIPHOSPHONATE

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Inventor(s): SUGIYAMA IWAKICHI; KASAI KOUSEI; TAKAOKA YUKIHISA;
HIJIKATA MAMORU +

Applicant(s): MATSUMOTO SEIYAKU KOGYO KK +

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Abstract of JP 51143620 (A)

PURPOSE: Epoxyester of hypophosphoric acid of formula I (where R is hydrocarbon residue), e.g. diglycidylether of 1-hydroxyethane-1, 1hypophosphoric acid II.

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① 日本国特許庁

公開特許公報

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発 明 の 名 称

エポキシジホスホネートの製造法

特許請求の範囲に記載された発明の数 2

発 明 者 ナラン ノンデバウ
千葉県習志野市袖ヶ浦3-5-2-410
スギヤマ 岩 吉
(ほか3名)

特 許 出 願 人

千葉県市川市南八幡5丁目13番2号

松本製薬工業株式会社

代表者 松本 伊兵衛

代 理 人 (郵便番号100)

東京都千代田区丸の内三丁目2番3号

(電話東京(211)2321大代表)

4230 弁 理 士 猪 股 清
(ほか2名)

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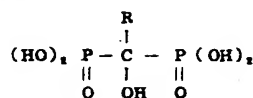
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C09J 3/1411
C09D 5/18
C09D 3/58
B01J 31/02

明 細 書

発明の名称 エポキシジホスホネートの製造法

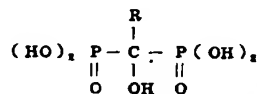
特許請求の範囲

(1) 一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸もしくはその部分中和された酸性塩に、分子中に二個以上のオキシラン基を有するポリエポキシ化合物一種もしくは二種以上を、前記リン酸中のPOH基と少なくとも等モル量反応させることを特徴とする、前記一般式で表わされるジリン酸のエポキシエステルの製造法。

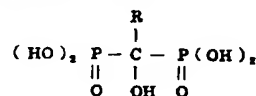
(2) 一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸、その酸性塩もしくはその中性塩に、エピハロヒドリンを反応させ、次いで前二者の場合はアルカリ処理を行なうことを特徴とする、前記一般式で表わされるジリン酸のエポキシエステルの製造法。

発明の詳細な説明

本発明は、一般式



(式中Rは炭化水素基を示す)で表わされるジリン酸の新規なエポキシエステルの製造法に関するものである。

接着剤、電気絶縁材料、塗料等の分野ではエポキシ樹脂が広く利用されて優れた性質を示している。しかしながら、これらエポキシ樹脂に対して期待される性能の全てが満足されているわけではない。たとえば電気絶縁材料や塗料、樹脂加工等

の分野では、安全管理の面から難燃化又は不燃化が要求されており、それに応じるためにハロゲン含有無水カルボン等の硬化剤やアンチモン、ハロゲン、リン等を含む難燃化剤を用いて改善を計る等の試みがなされているが、反応上添加量に自ら限度があり、必ずしも充分な効果を与えることはできない。また塗料の分野でも、エポキシ系化合物は他に比して比較的接着力が優れているが、防食性や耐久性を付与することは容易ではない。

一方、従来難燃性や防食性が望まれる分野では、種々のリン酸化化合物が使用されている。これらの多くはオルソ又はメタリン酸のエステル、つまりホスフェートかホスファイトであり、P-O-C結合、すなわちリン酸エステル結合から成るものである。これらとは別にP-O-C結合に比べて結合エネルギーの大きいP-C結合を有する化合物、たとえばホスホネートは化学的にも熱力学的にも安定性が大きく工業的に優れた性質を有することが期待できるが、ホスホネートは通常グリニャー反応、不飽和基へのホスフィン、ホスファイトの付

たキレート結合形成能があることから、水系接着剤、水系塗料、電気絶縁材料等の基材や各種組成物の難燃化剤としても有効であることを見出し、本発明に到達した。

本発明の前記一般式で表わされるジリン酸のエポキシエステルの製造法は、前記一般式で表わされるジリン酸もしくはその部分中和された酸性塩に、分子中に二個以上のオキシラン基を有するポリエポキシ化合物を、前記リン酸中のPOH基と少なくとも等モル量反応させて、一個のオキシラン基を付加させ、他のオキシラン基を残置させること、あるいは前記一般式で表わされるジリン酸もしくはその酸性塩にエビハロヒドリンを反応させたのちアルカリ処理してオキシラン形成を行なうこと、又は前記式Iで表わされるジリン酸の中性塩にエビハロヒドリンを反応させて脱塩反応させることを含むものである。

本発明に用いられる前記一般式で表わされるジリン酸は、Rがメチル、エチル等の低級アルキル基でも、ステアシル等の高級アルキル基でも、フ

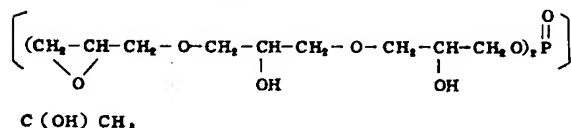
特開 昭51-143620 (2)
加反応、アルブゾブ反応等で合成しなければならず、反応条件の制約が大きいこと、反応工程が長いこと、反応に使用する各試剤の合成経路が長いこと等のために、製品コストが高く、またより限定した形の化合物しか得られず、広範な用途に適用するまでに到っていないのが現状である。

本発明者らは、安価でかつ安定性の高いホスホネートの製造と利用に関して種々研究を重ねた結果、先に酢酸又は塩化アセチルと隣酸又は三塩化リンとの反応で合成されるノ-ヒドロキシエタン-ノ、ノ-ジリン酸が特異な性能を有していることを知見した。このジリン酸は一般的には金属イオン封鎖剤、洗浄ビルダー、歯磨添加剤、無機スラリー添加剤等としての利用が提案されているが、本発明者らはこのジリン酸は金属に対してキレート形成反応を行なわせるのに適した骨格を有しており、また各種の化合物と反応して新規なキレート結合形成能を有する重合性不飽和ジリン酸を合成でき、これらのエポキシジリン酸化合物が、高いP含有量を有するため難燃性を与えやすく、ま

エニル等の環状炭化水素基であつてもよいが、生成物が水性であることを望む場合は、C₆以下が好ましい。たとえばノ-ヒドロキシエタン-ノ、ノ-ジリン酸、ノ-ヒドロキシプロパン-ノ、ノ-ジリン酸、ノ-ヒドロキシブタン-ノ、ノ-ジリン酸、ノ-ヒドロキシフェニルメタン-ノ、ノ-ジリン酸、ノ-ヒドロキシステアシルメタン-ノ、ノ-ジリン酸等が用いられる。

ポリエポキシ化合物としては、グリシジルエステル類、グリシジルーエーテル類等のグリシジル型エポキシ化合物、エポキシ化ポリオレフィン化合物、エポキシ化動植物油系化合物、環状脂肪族エポキシ化合物等が用いられ、個々の例としては、ジグリシジルエーテル、ブタンジオールジグリシジルエーテル、グリセリントリグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、ポリプロピレングリシジルエーテル、ビスフエノールA-ジグリシジルエーテル、ジベンタンジオキシド、シクロペンタンジエンジオキシド、ダイマー酸ジグリシジル、エポキシ化植物油、J、

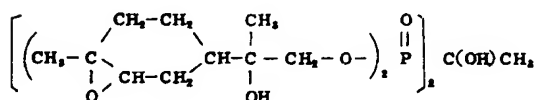
(19℃)であつた。反応生成物の一部を無水硫酸マグネシウムで脱水処理して得た生成物は、元素分析の結果P含有量6.39% (下記式としての計算値6.47%)、エポキシ当量339であり、赤外線吸収分析の結果、下記式の化合物に相当することが認められた。得られた生成物は水、メタノール、エタノールで精製できた。



実施例 - 3

1-ヒドロキシシブエニルメタン-1, 1-ジリン酸の40%水溶液67.0部に、グリセリンジグリシジルエーテル81.6部及びトリメチルベンジルアンモニウムクロリド0.1部を加えて攪拌し、これを80℃にて30分間加熱反応することにより淡黄色透明液体を得た。反応系のpHは反応前1以下であり、反応終了後5.7であつた。反応生成物の一部を無水硫酸で脱水処理して得た生成物は、元素

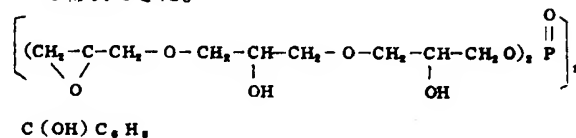
(下記式としての計算値7.04%)、エポキシ当量320であり、赤外線吸収分析の結果反応生成物は主として下記式に相当することが認められた。反応生成物はメタノール、エタノールに易溶性であつた。



実施例 - 5

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液34.3部に3, 4-エポキシ-6-メチルシクロヘキシルメチル-3, 4-エポキシ-6-メチルシクロヘキサンカルボキシレート112部、トリ-n-ブチルアミン0.2部を混合し、攪拌しつつ80℃に加熱し、30分間反応を行なつた。反応生成物は淡黄色液体であつた。生成物の一部をベンゼンで共沸脱水したのち過剰のベンゼンを留去し、淡黄色粘稠液体を得た。この液体の粘度は、14.5 PSであつた。脱水精製物の元素分析の結果、P

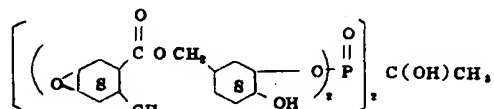
分析の結果P含有量5.78% (下記式としての計算値6.08%)、エポキシ当量355であり、赤外線吸収分析の結果下記式化合物に相当することが認められた。生成物は水、メタノール、エタノールで精製できた。



実施例 - 4

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液34.3部にジベンチンジオキシド67.2部、トリ-n-ブチルアミン0.1部、アルミニウムトリシアセチルアセトナート0.1部を加え、80℃に加熱して40分間反応を行つた。反応生成物の1部を採り無水硫酸マグネシウムで脱水精製して得られた生成物は、淡黄色透明な粘稠液体であり、粘度は12 PS (23℃)であつた。反応系のpHは反応前は1以下であり、反応終了後は4.3であつた。脱水精製物の元素分析の結果P含有量6.74%

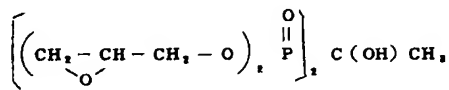
含有量4.31% (下記分子式としての計算値4.50%)、エポキシ当量345で赤外線吸収分析の結果主として下記に相当することが認められた。



実施例 - 6

1-ヒドロキシエタン-1, 1-ジリン酸の60%水溶液34.3部に、水酸化ナトリウム16部を水34部に溶解して加えて中和してNa₂塩とした。これにエビプロモヒドリン8部を加えて70℃で40分間反応を行なつて反応を終了した。反応生成物の一部を採り、これに過剰のトルエンを加えて脱水し、更にエビプロモヒドリンを減圧留去し、生成した塩を尹別して淡黄色粘稠液体を得た。粘度13.2 PS (18℃)であつた。この精製物の元素分析を行なつた結果、P含有量15.01% (下記式としての15.27%)、エポキシ当量103であり、ハロゲン

残留は微量であつた。これらの分析の結果、得られた生成物の構造は下式に相当することが認められた。



実施例 - 7

1-ヒドロキシエタン-1、1-ジリン酸の60%水溶液34.3部に、水酸化ナトリウム8部を水17部に溶解して加えて中和したのちエビプロモヒドリン28部を加えて80℃で40分間反応を行なつた。反応液は淡黄色透明であつた。これを30℃に下げ水酸化ナトリウム8.0部を水17部に溶解して加えて20分間攪拌したのち、更に60~70℃に加熱して40分間反応を行なつた。反応終了後のpHは7.6であつた。反応生成物のエポキシ当量は43.5であり、この反応液40部にトリエチレントトラミン4部を加えたところ、室温で30分後60℃に昇温し、淡黄色透明の含水樹脂を与えた。この樹脂はバーナーから外すと直ちに消火し、難燃性であつた。

シジホスホネート10部をそれぞれ下記第1表に示されるエポキシ硬化剤により硬化難燃性樹脂を製造した(それぞれ参考例1~4)。得られた樹脂の燃焼性を第1表に示す。

第 1 表

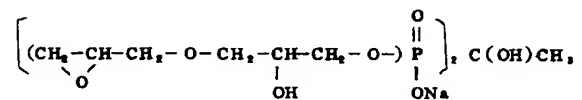
	硬 化 剤	硬化時間(分)	燃 焼 性
参考例1	ジエチレントリアミン 2部	25	バーナーから外すと直ちに消火
" 2	" 2.5部	20	"
" 3	トリエチレントトラミン 2.5部	15	"
" 4	" 1.5部	20	"

参考例 - 5

実施例 - 5の生成物15部にヘキサメチレンジアミン3部を加えて充分攪拌し、下記第2表に示す材質での接着試験を行なつた結果、いずれも木破が発生し、良好であつた。また硬化した樹脂はバーナーから外すと直ちに消火し難燃性であつた。

実施例 - 8

1-ヒドロキシエタン-1、1-ジリン酸の60%水溶液34.3部に水酸化ナトリウム8部を水17部に溶解して攪拌下に滴下反応させ1-ヒドロキシエタン-1、1-ジリン酸2ナトリウム塩水溶液を得た。これにジグリシジルエーテル26.5部を加え、80℃で50分間反応して淡黄色透明粘稠液を得た。反応終了時の溶液のpHは6.9であつた。反応生成物の一部を採り脱水精製して得た生成物はPの元素分析の結果、P含有量11.94%(下配式としての計算値12.15%)、赤外線吸収分析の結果下配式に相当することが認められた。生成物は水、メタノールに可溶であり、トリエチレントトラミンで硬化し淡黄色透明の難燃性樹脂を与えた。



参考例 - 1~4

実施例1~4において合成された新規なエポキシ

第 2 表

材 質	養生条件	引張・剪断強度(N)
ラワン合板 - 軟 鋼	25℃, 24時間, 60% pH	115
ラワン合板 - ラワン合板	" " "	121

* 5mm厚、1級

25mm幅 × 125mm長さ

出願人代理人 猪 股 清

添 附 書 類 の 目 録

- | | |
|-----------|-----|
| (1) 明 細 書 | 1 通 |
| (2) 図 面 | 1 通 |
| (3) 委 任 状 | 1 通 |

前記以外の発明者、特許出願人または代理人

発 明 者

千葉県市川市平田 1 - 13 - 3
登 井 孝 正

茨城県稲敷郡牛久町柏田 3612
高 岡 肇 久

東京都江東区北砂 6 - 7 - 14
土 方 守

代 理 人 (郵便番号 100)

東京都千代田区丸の内三丁目2番3号

3202	弁 理 士	佐 藤 勇 吉
同 所		
6285	同	野 一 色 道 夫
同 所		
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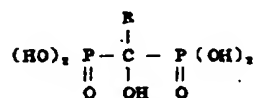
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 C09D 3/58
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 (22) Application Date: June 6, 1975
 (71) Applicant: MATSUMOTO SEIYAKU KYOGYO KK
 (72) Inventor: SUGIYAMA Iwakichi
 KASAI Takamasa
 15 TAKAOKA Yukihiisa
 HIJIKATA Mamoru
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SPECIFICATION

- 20 TITLE OF THE INVENTION
 Process for preparation of epoxydiphosphonate

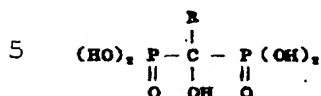
CLAIMS

1. A process for preparing an epoxyester of a diphosphonic
 25 acid represented by the following formula:



- wherein R represents a hydrocarbon group,
 30 the process comprising:
 allowing the diphosphonic acid represented by the above
 formula or a partially neutralized acid salt thereof to react
 with one or two or more polyepoxy compounds having two or more
 oxirane groups in the molecular structure in a molar amount at
 35 least equivalent to that of the POH group in the phosphonic acid.

2. A process for preparing an epoxyester of a diphosponic acid represented by the following formula:



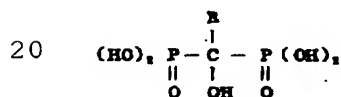
wherein R represents a hydrocarbon group,
the process comprising:

allowing the diphosponic acid represented by the above
10 formula, an acid salt or a neutral salt thereof to react with
an epihalohydrin; and

treating the resulting product with an alkali if one of
the former two is used.

15 DESCRIPTION OF THE INVENTION

The present invention relates to a process for preparing
a novel epoxyester of a diphosponic acid represented by the
following formula:



wherein R represents a hydrocarbon group.

Epoxy resins have been widely used in adhesive agents,
electric insulation materials, coatings, and the like, and
25 exhibit high performance. Epoxy resins, however, fail to
satisfy required levels in some properties. For example, for
electric insulation materials and coatings, and processing of
resins, properties of flame retardance and incombustibility are
required for safety. There have been some studies conducted
30 to satisfy this demand. In these studies, a curing agent such
as anhydrous halogen containing-carvone, a flame retardant
containing antimony, a halogen, phosphorus, or the like are used
to improve the properties. In order to allow the reaction to
proceed, these substances cannot be added in amounts over
35 certain levels, and thereby do not necessarily produce

sufficient effects. When used in a coating, epoxy compounds show relatively excellent adhesivity compared to other materials; however, it is difficult to provide anti-corrodibility and durability to the coating with the epoxy compounds.

In fields in which flame retardance and anti-corrodibility are required, phosphoric acid compounds of various types have been conventionally used. Most of these are esters of ortho- or metaphosphoric acids, that is, phosphates and phosphites, and include a P-O-C bond or a phosphonic acid ester bond. Apart from these compounds, compounds having a P-C bond, which has a higher bond energy than that of the P-O-C bond, such as phosphonates are chemically and thermodynamically stable, and are expected to show industrially favorable performance. Phosphonates are typically synthesized through a reaction such as the Grignard reaction, an addition reaction of a phosphine or phosphite to an unsaturated group, or the Arbuzov reaction. In these reactions, reaction conditions are restricted, the reaction processes requires a long time, and synthesis paths of reagents used in the reaction are long. For these and other reasons, the product cost is high. In addition, products through such a reaction have a configuration of some determined type. Therefore, these compounds have not been widely used.

The present inventors studied on preparation and use of inexpensive and stable phosphonate to find specific performance of 1-hydroxyethane-1,1-diphosphonic acid synthesized through the reaction between acetic acid or acetyl chloride, and phosphoric acid or trichlorophosphate. This diphosphonic acid have been typically proposed for use in metal ion blocking agents, detergent builders, additives for dentifrices, additives for inorganic slurries, and the like. The present inventors, however, focused on the characteristics and properties of this diphosphonic acid that this diphosphonic acid has the skeleton capable of easily reacting with a metal

to form a chelate, that this diphosphonic acid easily synthesizes novel polymeric unsaturated diphosphoric acids capable of forming a chelate bond with compounds of various types, that these epoxy diphosphoric acid compounds easily
5 provide flame retardance owing to its high P content, and that these epoxy diphosphoric acid compounds are capable of forming a chelate bond. Considering these facts, the present inventors found that these epoxy resin compounds are advantageously used as base materials in aqueous adhesive agents, aqueous coatings,
10 electric insulation materials and the like, and as flame retardants for various compounds. Thus, the present inventors completed the present invention.

The process for preparing an epoxyester of a diphosphonic acid represented by the above formula of the present invention
15 includes a step of allowing a diphosphonic acid represented by the above formula or a partially neutralized acid salt thereof to react with polyepoxy compounds having two or more oxirane groups in the molecular structure in a molar amount at least equivalent to that of the POH group in the phosphoric acid so
20 that one of the oxirane groups is lost by the addition reaction and the other oxirane groups are remained; steps of allowing a diphosphonic acid represented by the above formula or an acid salt thereof to react with an epihalohydrin, and treating the resulting product with an alkali to form an oxirane; or a step
25 of allowing a neutral salt of a diphosphonic acid represented by the above formula I to react with an epihalohydrin so that the desalt reaction occurs.

In diphosphonic acids represented by the above formula used in the present invention, R may be a lower alkyl group such
30 as methyl or ethyl group, a higher alkyl group such as stearyl group, or a cyclic hydrocarbon group such as phenyl group. However, in order to yield an aqueous product, R is preferably a group having not more than eight carbon atoms. Examples thereof include 1-hydroxyethane-1,1-diphosphonic acid,
35 1-hydroxypropane-1,1-diphosphonic acid,

1-hydroxybutane-1,1-diphosphonic acid,
1-hydroxyphenylmethane-1,1-diphosphonic acid, and
1-hydroxystearyl methane-1,1-diphosphonic acid.

Examples of the polyepoxy compounds include glycidyl
5 epoxy compounds such as glycidyl esters and glycidyl ethers,
epoxidized polyolefin compounds, epoxidized animal or
vegetable oils, and alicyclic epoxy compounds. Specific
examples of these include diglycidyl ether, butanediol
diglycidyl ether, glycerin triglycidyl ether, polyethylene
10 glycol diglycidyl ether, polypropylene glycidyl ether,
bisphenol A diglycidyl ether, dipenthen dioxide, cyclopentane
diene dioxide, diglycidyl esters of dimer acids, epoxidized
vegetable oils,
3,4-epoxycyclohexyl-3,4-epoxycyclocarboxylate.

15 In the reaction between a diphosphonic acid represented
by the above formula and polyepoxy compounds, the polyepoxy
compounds are used in an amount of 4 mol or more with respect
to 1 mol of the diphosphonic acid. If a partially neutralized
acid salt such as an alkaline metal salt or an ammonium salt
20 of a diphosphonic acid is used, the polyepoxy compounds are
preferably used in a molar amount equivalent to or more than
that of the POH group. The conditions for the reaction are not
particularly limited, and it is preferable that a diphosphonic
acid or a salt thereof is added to polyepoxy compounds. In this
25 case, if the molar amount of polyepoxy compounds is less than
the molar amount of the POH group, the polymerization reaction
may occur. The reaction temperature is from room temperature
to 100°C. A compound that effectively serves as an
epoxy-ring-opening catalyst such as a tertiary amine,
30 quaternary amine, boron complex, or metal complex may be used,
if necessary. Examples of particularly preferable catalysts
include triethylamine, tri-n-butylamine, pyridine,
dimethylaniline, N,N-dimethyl para-toluidine, trimethyl
benzil ammonium chloride, dodecylpyridinium chloride,
35 trifluoroboron etherate, ferrocene, titanocene, zirconocene,

ammonium tris acetylacetonato, and zirconium tetrakis acetylacetonato.

Examples of epihalohydrins used in the present invention include epichlorohydrin, epibromohydrin, and halogenated
5 alcohol glycidyl ether such as
1-(1-chloro-2-hydroxypropoxy)-butane-4-glycidyl ether, and
2-chloroethyl-1-glycidyl ether.

In the reaction involving a neutral salt of a diphosphonic acid represented by the above formula such as a salt with an
10 alkaline metal, for example, lithium, sodium or potassium, or
a salt with an amine, for example, a tertiary amine, an
epihalohydrin is used in an amount of 2 to 4 mol with respect
to 1 mol of the diphosphonic acid to desalt and epoxidize the
salt. In the reaction between a diphosphonic acid represented
15 by the above formula or an acid salt thereof and an epihalohydrin,
the epihalohydrin is used in an amount of 2 to 4 mol with respect
to 1 mol of the diphosphonic acid or the acid salt thereof to
allow the addition reaction to occur. Subsequently, the
resulting product is treated with an alkaline compound such as
20 lithium hydroxide, sodium hydroxide, potassium hydroxide,
sodium carbonate, potassium carbonate, or potassium acetate so
that the halohydrin group is desalted and the ring is closed.

Epoxy esters of diphosphonic acids represented by the
above formula produced as described above are excellent in
25 ability to form a chelate with a metal, and easily achieve flame
retardance. Application of such epoxy esters in wide
industrial fields is demanded. These compounds are suitably
used as flame retardant epoxy resin base materials or epoxy base
materials capable of forming a chelate bond in adhesive agents,
30 resins, coatings, and the like.

Hereinafter, examples of the present invention are
described. The units "part" and "%" in examples are based on
weight.

35 Example 1

20

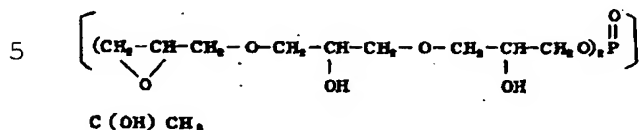


Example 2

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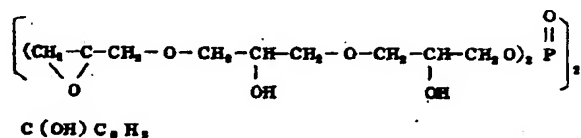
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absorption analysis revealed that the product corresponds to the compound represented by the following formula. The obtained product was diluted with water, methanol or ethanol.



Example 3

10 An amount of 81.6 parts of glycerin diglycidyl ether and 0.1 parts of trimethylbenzyl ammonium chloride were added to 67.0 parts of 40% aqueous solution of 1-hydroxyphenylmethane-1,1-diphosphonic acid, and the mixture was stirred. Then, the mixture was allowed to react while being
15 heated to 80°C for 30 minutes to yield a transparent light yellow liquid. The pH of the reaction system was not higher than 1 before the reaction, and was 5.7 after the reaction. Portion of the reaction product was dehydrated with anhydrite sodium sulfate to yield a product. The results of the elemental
20 analysis on the product showed that the product had a P content of 5.78% (6.08 % calculated based on the following formula), and an epoxy equivalent of 225. The infrared absorption analysis revealed that the product corresponds to the compound represented by the following formula. The obtained product was
25 diluted with water, methanol or ethanol.

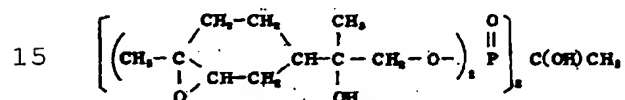


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Example 4

An amount of 67.2 parts of dipenthen dioxide, 0.1 parts of tri-n-butylamine and 0.1 parts of aluminum tris acetylacetonato were added to 34.3 parts of 60% aqueous solution
35 of 1-hydroxyethane-1,1-diphosphonic acid. The mixture was

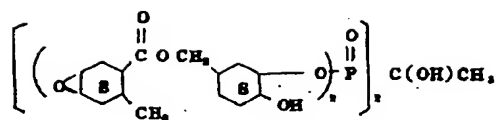
heated to 80°C, and the reaction was allowed to proceed for 40 minutes. Portion of the reaction product was dehydrated and purified with anhydrite magnesium sulfate to provide a product. The product was a transparent light yellow sticky fluid and had a viscosity of 12 PS (23°C). The pH of the reaction system was not higher than 1, and was 6.3 after the reaction. The results of the elemental analysis on the purified dehydrated product showed that the product had a P content of 6.74% (7.06% calculated based on the following formula), and an epoxy equivalent of 220. The infrared absorption analysis revealed that the reaction product mainly corresponds to the compound represented by the following formula. The obtained product was easily soluble in methanol or ethanol.



Example 5

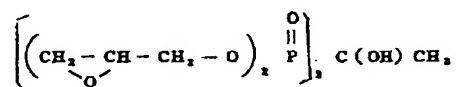
An amount of 112 parts of 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate and 0.2 parts of tri-n-butylamine were added to 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid, and the mixture was heated to 80°C under stirring. The reaction was allowed to proceed for 50 minutes. The reaction product was a light yellow liquid. Portion of the product was azeotropically dehydrated with benzene, and excessive benzene was removed to provide a light yellow sticky fluid. The fluid had a viscosity of 14.5 PS. The results of the elemental analysis on the purified dehydrated product showed that the product had a P content of 4.31% (4.50% calculated based on in the following formula), and an epoxy equivalent of 345. The infrared absorption analysis revealed that the product mainly corresponds to the compound represented by the following formula.

35



5 Example 6

An amount of 16 parts of sodium hydride dissolved in 34 parts of water was added to neutralize 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid to yield the Na salt. An amount of 83 parts of epibromohydrin was added to the salt, and the reaction was allowed to proceed at 70°C for 40 minutes, and then terminated. Portion of the reaction product was dehydrated with toluene, and epibromohydrin in the product was removed in vacuo to provide the salt. The obtained salt was filtered off to provide a light yellow sticky fluid. The fluid had a viscosity of 13.2 PS (18°C). The results of the elemental analysis on the purified product showed that the product had a P content of 15.01% (15.27% calculated based on the following formula), and an epoxy equivalent of 102. Only a slight amount of the halogen was remained therein. The analysis revealed that the structure of the product corresponds to the following formula.



25

Example 7

An amount of 8 parts of sodium hydride dissolved in 17 parts of water was added to neutralize 34.3 parts of 60% aqueous solution of 1-hydroxyethane-1,1-diphosphonic acid. Thereafter, 28 parts of epibromohydrin was added thereto, and the reaction was allowed to proceed at 80°C for 40 minutes. The reaction fluid was transparent light yellow. The reaction liquid was cooled to 30°C, and 8.0 parts of sodium hydride dissolved in 17 parts of water was added to the reaction liquid, and the resulting mixture was stirred for 20 minutes. The

35

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Example 8

15



Reference examples 1 to 4

An amount of 10 part of each of the novel epoxy

diphosphonates prepared in Examples 1 to 4 was cured with the epoxy curing agent shown in Table 1 to provide cured flame retardant resins (each assigned to Reference examples 1 to 4). Table 1 shows the flame retardance of the obtained resins.

5

Table 1

	Curing agent	Curing time (min)	Incombustibility
Reference example 1	Diethylenetriamine 2 parts	25	Fire disappeared immediately after removal from a burner.
Reference example 2	Diethylenetriamine 2.5 parts	20	Fire disappeared immediately after removal from a burner.
Reference example 3	Triethylenetetramine 2.5 parts	15	Fire disappeared immediately after removal from a burner.
Reference example 4	Triethylenetetramine 1.5 parts	20	Fire disappeared immediately after removal from a burner.

Reference example 5

10 An amount of 3 parts of hexamethylenediamine was added to 15 parts of the product obtained in Example 5, and the resulting mixture was sufficiently stirred. An adhesion test was performed using the materials shown in Table 2. Favorable results were obtained in either case, that is, the wood materials were broken. Fire disappeared immediately after the
15 cured resin was removed from the burner, indicating that the cured resin was flame retardant.

20

Table 2

Material	Curing condition	Tensile strength, shear strength (kg/cm ²)
Lauan plywood*- soft steel	25°C, 24 hours, 60% pH	115
Lauan plywood- lauan plywood	Same as above	121

*Thickness: 5mm, First grade

25 mm width x 125 length